Radiochim. Acta 84, 111–114 (1999)

Rapid Communication

Complexation of Radionuclides with Humic Substance: The Metal Concentration Effect

By W. Hummel, M. A. Glaus and L. R. Van Loon

Paul Scherrer Institut, Waste Management Laboratory, CH-5232 Villigen PSI, Switzerland

(Received September 27, 1998; accepted in revised form January 28, 1999)

Humic substance / Complexation / Metal concentration / Performance assessment

Summary

A synopsis of experimental data concerning the complexation of radionuclides with humic substance from various laboratories using different experimental methods reveals a consistent pattern of the metal concentration effect: With decreasing radionuclide concentration (and all other parameters held constant) an increase in the complexation of the radionuclide with humic substance is observed. The implications of this effect for model calibration and practical applications are discussed.

1. Introduction

The complexation of radionuclides with humic substance has been investigated for three decades by various laboratories using different experimental methods over a wide range of experimental parameters. The reported results, mostly given in terms of "complexation constants" or "stability constants" of some sort, vary considerably. In a recent study of the complexation of Np(V) with humic acid [1] the authors made an intercomparison of results from different laboratories. They conclude that there are two primary reasons for the observed variation in reported complexation constants: large uncertainties and systematic errors in certain experimental methods, and different approaches of evaluating the concentration of free humic acid. We agree that some of the observed scatter in reported complexation constants can be ascribed to artefacts and uncertainties in experimental procedures. Also calculations of the concentration of free humic acid by different authors may be based on different model assumptions and operational definitions. This certainly is a source of sometimes large variations in comparisons of reported numerical results, even if the original experimental data show very good agreement. However, the main reason for the observed differences is not a matter of definitions and systematic experimental artefacts, but stems from the fact that the measurements, while using different experimental methods, span a large range, not only in pH but also in metal concentration. In the following we will visualize the influence of varying metal concentration on the results by a synopsis of experimental data measured by several different techniques in a number of laboratories [1, 2*, 4–14].

2. Synopsis of experimental data

The minimal set of experimental data needed to describe the interaction of a metal ion, M, with a humic substance, HS, comprises [MHS], the concentration of metal bound to a certain humic substance, [M], the concentration of free metal in the aqueous phase, and $(HS)_{total}$, the total concentration of humic substance. [MHS] and [M] can be quantified on the molar scale [mol/L], but $(HS)_{total}$ is known only as mass per unit volume (g/L). Note, that [] is used in the following for molarity units and () for mass per unit volume.

This minimal set of experimental information can be summarized by a constant ^{c}K, defined as the number of moles of metal bound per gram of humic substance divided by the concentration of free metal in solution:

$$^{c}K = \frac{[MHS]}{[M] \cdot (HS)_{total}} . \quad (1)$$

The unit of ^{c}K therefore is volume per mass, usually given as L/g.

In contrast to simple organic ligands with known molecular structure, "humic substance" serves just as a label for an operationally defined class of a naturally occurring mixture of medium to large size molecules. Any attempt to calculate the concentration of free humic substance (i.e. the concentration of free binding sites) involves additional model assumptions or additional operational definitions, such as a mean molecular weight, a proton exchange capacity, the degree of proton dissociation, or a loading capacity. These different assumptions and definitions invariably lead to different values for the concentration of free binding

* All experimental raw data published in [2] are also available on the Internet under the address http://www.psi.ch by chosing "Departments and Projects" and "Waste Management".

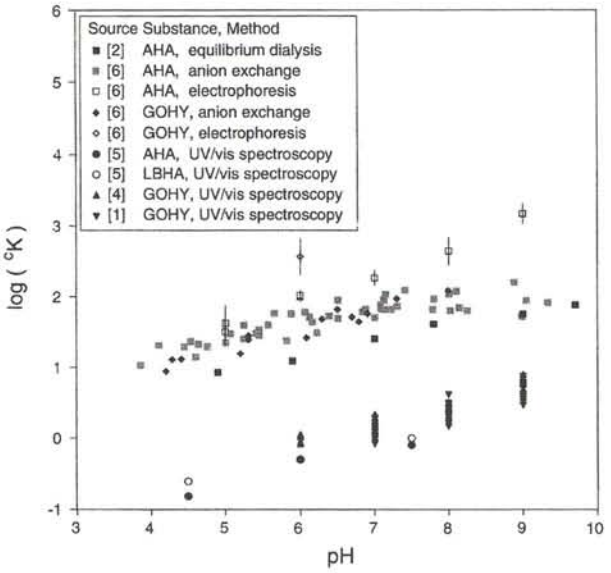

Fig. 1. Synopsis of the pH dependence of published Np(V) complexation data of various humic acids obtained by different experimental methods. Abbreviations are: AHA Aldrich humic acid, GOHY Gorleben GOHY-573 humic acid, LBHA Lake Bradford humic acid. In cases where a set of experimental data has been averaged, error bars (1 σ) are shown.

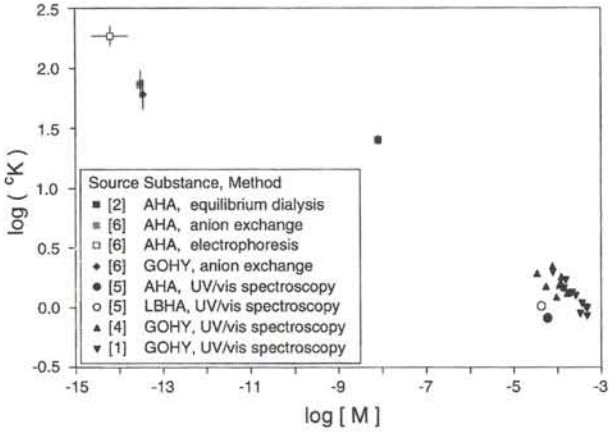

Fig. 2. Np(V) complexation data of various humic acids obtained by different experimental methods: Metal concentration effect in the pH range 7.0–7.5. Abbreviations are: AHA Aldrich humic acid, GOHY Gorleben GOHY-573 humic acid, LBHA Lake Bradford humic acid. In cases where a set of experimental data has been averaged, error bars (1 σ) are shown.

sites and thus result in different values for complexation constants. Hence, as discussed in detail in [3], the concentration of free binding sites is a model dependent parameter. In order to avoid ambiguities due to this model dependent parameter, for the following intercomparisons all experimental data were re-evaluated according to Eq. (1) and given as log ^{c}K values.

In this contribution we will not discuss the effect of different water compositions on radionuclide-humic complexation, i.e. the effect of competing cations like Ca or Al on radionuclide complexation is neglected. Therefore we only compare data measured in NaCl [7], KNO_3 [8] or $NaClO_4$ solutions (all other references).

2.1 Np(V)

A synopsis of experimental data concerning the complexation of Np(V) with humic substance is shown in Fig. 1 as a plot of log ^{c}K versus pH. As can be seen in this plot, the data cluster essentially in two regions of log ^{c}K. Data in the lower cluster, determined by UV/vis spectroscopy by two different groups [1, 4, 5], show good overall agreement. Data in the upper cluster, determined by equilibrium dialysis [2], electrophoretic ion focusing and anion exchange [6], exhibit somewhat larger scatter. In Fig. 1 all data points are recalculated from experimental values according to Eq. (1). Hence, the separation of data into two clusters does not arise due to different definitions of complexation constants. In [1] it was concluded that the only alternative explanation for such divergence may lie in the experimental methods. The authors state that the large discrepancy in the results is hardly ascribed to their spectroscopic method and therefore, the observed discrepancy may be attributable to large uncertainties in the other experimental methods. Indeed, some of the scatter seen in the upper data cluster of Fig. 1 may arise from uncertainties in experimental methods but the main features reflect real chemical effects. Fig. 1 is a two-dimensional projection of a multi-dimensional chemical parameter space. The most important parameter not considered in Fig. 1 is the concentration of the radionuclide. If we take a "slice" of data from Fig. 1 in the pH range 7 to 7.5, where results from all different sources overlap, and plot log ^{c}K versus log [M], the concentration of free Np(V), the metal concentration effect is immediately revealed (Fig. 2). All measurements by UV/vis spectroscopy were done at high metal concentration (10^{-4} M and higher), whereas the measurements by equilibrium dialysis were carried out at 10^{-8} M Np(V) and the measurements by electrophoretic ion focusing and anion exchange were done in the range of 10^{-13} M. The consistent picture revealed by Fig. 2 (and similar pictures can be found for any "pH slice") indicates a strong dependence of the experimental ^{c}K values on the radionuclide concentration. With decreasing metal concentration a significant increase in the complexation of the metal by humic substance is observed.

2.2 Ca

This observation is not restricted to Np(V). Another example is shown in Fig. 3 where experimental data of Ca complexation with humic substance is assembled. Again, data measured by three different methods, equilibrium dialysis [2], Schubert's ion exchange method [7] and measurements with a Ca sensitive electrode [8], reveal a consistent picture. With decreasing metal

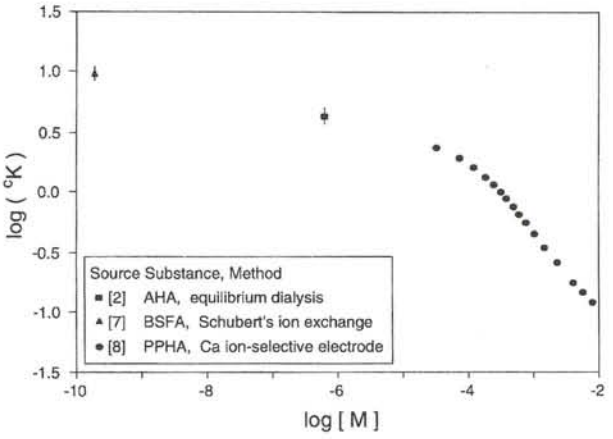

Fig. 3. Ca complexation data of humic and fulvic acids obtained by different experimental methods: Metal concentration effect in the pH range 6.0−6.7. Abbreviations are: AHA Aldrich humic acid, BSFA Broubster Sepragen fulvic acid, PPHA Purified peat humic acid. In cases where a set of experimental data has been averaged, error bars (1 σ) are shown.

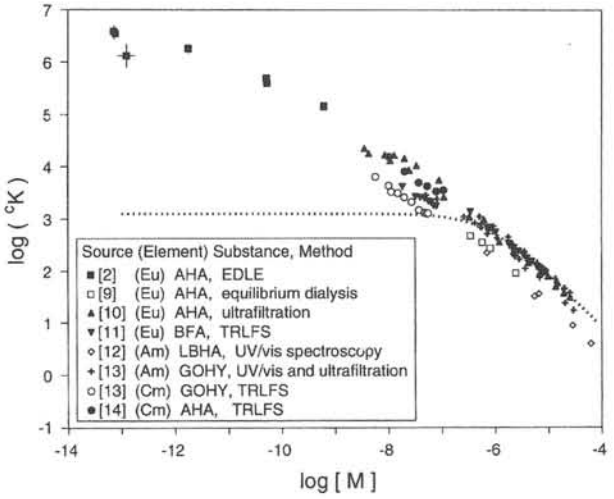

Fig. 4. Eu, Am and Cm complexation data of humic and fulvic acids obtained by different experimental methods: Metal concentration effect in the pH range 5.0−5.5. Abbreviations are: AHA Aldrich humic acid, BFA Bersbo fulvic acid, GOHY Gorleben GOHY-573 humic acid, LBHA Lake Bradford humic acid, EDLE Equilibrium dialysis-ligand exchange, TRLFS Time-resolved laser-fluorescence spectroscopy. In cases where a set of experimental data has been averaged, error bars (1 σ) are shown. The dotted line represents model calculations according to the model discussed and calibrated in [13].

concentration the complexation of Ca with humic substance becomes more pronounced in a very systematic manner.

2.3 Eu, Am, Cm

In the cases of Np(V) and Ca discussed so far, the overall metal concentration effect in the investigated concentration range is found to be less than two orders of magnitude in °K. However, in the cases of the trivalent cations Eu, Am and Cm the metal concentration effect is much more pronounced. A synopsis of experimental data from different laboratories, measured with different methods and comprising different humic substances reveals a very consistent pattern (Fig. 4). (Note, that the Cm data from [13] were re-evaluated starting with the raw experimental data given in Fig. 3 in [13] and using the same evaluation method as outlined in [11] and used in [14]. The values of $[Cm^{3+}]$ and [CmHA(II)] given in Table 5 of [13], corresponding to [M] and [MHS] in our nomenclature, are the result of fitting the raw data to the humic complexation model of [13].) The scatter in experimental data from different sources does not exceed one order of magnitude in °K (Fig. 4) if data within a certain narrow range of metal concentration is considered. This is consistent with the observations for Ca (Fig. 3) and Np(V) (Fig. 2). However, the overall systematic variation in °K as a function of free metal concentration spans several orders of magnitude.

3. Conclusions

Summarizing our results revealed by a synopsis of experimental data, we conclude that there is ample evidence of a metal concentration effect concerning the complexation of radionuclides with humic substance. The observation of such an effect is not surprising if we consider "humic substance" as a mixture of molecules. Some binding sites of these molecules are expected to exhibit stronger affinity to metal ions than others. These strong binding sites determine the metal uptake at very low metal concentrations. With increasing metal concentration the strong sites reach saturation and weaker binding sites determine the metal uptake resulting in an overall decrease of metal-humate interaction with increasing metal concentration. This conceptual view of metal complexation by humic substance is widely accepted in the literature [8, 15, 16] and the discussions generally do not address the metal concentration effect as such but concern the question how this effect could be adequately described by humic binding models. A recently proposed pragmatic approach for application in the field of performance assessment for repositories of radioactive waste is discussed in detail in [2]. For a review of binding models with respect to the effects of metal concentration, pH and ionic strength see [3]. However, any model may underestimate the metal-humate interaction by several orders of magnitude (e.g. dotted line in Fig. 4) if the model is calibrated only at high metal concentration and subsequently used for calculations at very low metal concentration. Hence, consideration of the metal concentration effect is of utmost importance in any practical application aiming at an assessment of the influence of humic substance on the complexation and mobility of traces of radionuclides escaping an underground repository.

Acknowledgements

Partial financial support by Nagra is gratefully acknowledged. The authors would like to thank Drs.

F. J. Pearson Jr., J. Hadermann and an anonymous reviewer for giving useful suggestions to improve the text.

References

1. Marquardt, C., Kim, J. I.: Complexation of Np(V) with Humic Acid: Intercomparison of Results from Different Laboratories, Radiochim. Acta **80**, 129 (1998).
2. Glaus, M. A., Hummel, W., Van Loon, L. R.: Experimental Determination and Modelling of Trace Metal-Humate Interactions: A Pragmatic Approach for Applications in Groundwater, PSI Bericht Nr. 97-13, Paul Scherrer Institut, Villigen, Switzerland (1997) pp. 251.
3. Hummel, W.: Binding Models for Humic Substances. In: *Modelling in Aquatic Chemistry*, Grenthe, I. and Puigdomènech, I., Eds., OECD Nuclear Energy Agency, Paris (1997), Chap. V.
4. Kim, J. I., Sekine, T.: Complexation of Neptunium(V) with Humic Acid, Radiochim. Acta **55**, 187 (1991).
5. Rao, L., Choppin, G. R.: Thermodynamic Study of the Complexation of Neptunium(V) with Humic Acids, Radiochim. Acta **69**, 87 (1995).
6. Marquardt, C., Herrmann, G., Trautmann, N.: Complexation of Neptunium(V) with Humic Acids at Very Low Metal Concentrations, Radiochim. Acta **73**, 119 (1996); and Marquardt, C.: Wechselwirkung von Neptunium(V) in sehr geringen Konzentrationen mit Huminsäure, Dissertation, Universität Mainz (1994).
7. Higgo, J. J. W., Davies, J., Smith, B., Din, S., Crawford, M. B., Tipping, E., Falck, W. E., Wilkinson, A. E., Jones, M. N., Kinniburgh, D.: Comparative Study of Humic and Fulvic Substances in Groundwaters: 3. Metal Complexation with Humic Substances, British Geological Survey, Technical Report WE/92/12, Wallingford, UK (1992).
8. Benedetti, M. F., Milne, C. J., Kinniburgh, D. G., van Riemsdijk, W. H., Koopal, L. K.: Metal Ion Binding to Humic Substances: Application of the Non-Ideal Competitive Adsorption Model, Environ. Sci. Technol. **29**, 446 (1995).
9. Carlsen, L., Bo, P., Larsen, G.: Radionuclide – Humic Acid Interactions Studied by Dialysis. In: *Geochemical Behavior of Disposed Radioactive Waste*, Barney, G. S., Navratil, J. D., Schulz, W. W., Eds., American Chemical Society, Washington, DC (1984), p. 167–180.
10. Caceci, M. S.: The Interaction of Humic Acid with Europium(III). Complexation Strength as a Function of Load and pH, Radiochim. Acta **39**, 51 (1985).
11. Bidoglio, G., Grenthe, I., Qi, P., Robouch, P., Omenetto, N.: Complexation of Eu and Tb with Fulvic Acids as Studied by Time-Resolved Laser-Induced Fluorescence, Talanta **38**, 999 (1991).
12. Kim, J. I., Buckau, G., Bryant, E., Klenze, R.: Complexation of Americium(III) with Humic Acid, Radiochim. Acta **48**, 135 (1989).
13. Kim, J. I., Rhee, D. S., Wimmer, H., Buckau, G., Klenze, R.: Complexation of Trivalent Actinide Ions (Am^{3+}, Cm^{3+}) with Humic Acid: A Comparison of Different Experimental Methods, Radiochim. Acta **62**, 35 (1993).
14. Moulin, V., Tits, J., Moulin, C., Decambox, P., Mauchien, P., de Ruty, O.: Complexation Behaviour of Humic Substances towards Actinides and Lanthanides Studied by Time-Resolved Laser-Induced Spectrofluorometry, Radiochim. Acta **58/59**, 121 (1992).
15. Buffle, J., Altmann, R. S., Filella, M., Tessier, A.: Complexation by Natural Heterogeneous Compounds: Site Occupation Distribution Functions, a Normalized Description of Metal Complexation, Geochim. Cosmochim. Acta **54**, 1535 (1990).
16. Tipping, E., Hurley, M. A.: A Unifying Model of Cation Binding by Humic Substances, Geochim. Cosmochim. Acta **56**, 3627 (1992).